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NEW DEVELOPMENTS IN HYDROGEN PERMSELECTIVE MEMBRANES

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DISCLAIMER

9b.3 New Developments in Hydrogen Permselective Membranes

CONTRACT INFORMATION

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OBJECTIVES

The objectives of the original project was to develop silica hydrogen permselective membranes and evaluate the economic feasibility of these membranes in hydrogen production from coal gas. The objectives of the work reported here were to increase the membrane permeance by developing new precursors or deposition conditions, and to carry out fundamental permeability measurements of the membrane at different stages of pore narrowing.

BACKGROUND INFORMATION

In the work performed under the above referenced METC contract[1-3], the contractor developed hydrogen permselective membranes by chemical vapor deposition (CVD) of thin SiO_2 layers within the pores of Vycor tubes having mean pore diameter about 40 Å. The hydrogen permeance after CVD was about 0.35 cm^3/cm^2-min-atm versus about 0.5 for the original tube, both at 500°C, so that the resistance due to the deposit layer was 30% of the total resistance. To test their stability under conditions simulating the expected operating conditions in coal gas processing, the membrane tubes were heated under 3 atm of water vapor (and 7 atm N_2) at 550°C for up to 21 days. During this hydrothermal treatment the hydrogen permeance declined and stabilized to a value about 0.1 cm^3/cm^2-min-atm at 500°C. The stable membrane permeance represented 80% of the total resistance to hydrogen permeation. The H_2:N_2 selectivity after the hydrothermal treatment was in the range 500-1000.

To evaluate the economic feasibility of the silica membranes, KTI Inc. under subcontract to Caltech conducted a case study of an ammonia-from-coal process comparing a conventional process with a membrane-assisted process[2]. In the conventional process the coal gas was treated by catalytic water gas shift reaction followed by hydrogen separation by pressure swing adsorption (PSA). In the membrane-assisted process, hydrogen was separated simultaneously with the catalytic shift reaction, resulting in reduced consumption of steam and elimination of PSA. Although accurate capital costs for the hydrogen membrane were not available, approximate

estimates suggested that the membrane-assisted process would become competitive if the membrane permeance was increased from the then available 0.1 cm^3/cm^2-min-atm value to 0.3 cm^3/cm^2-min-atm.

In view of the results of the economic evaluation, a new project was undertaken to increase the hydrogen permeance of the silica membranes. This new project was supported by the DOE University Coal Research Program and by funds from internal Caltech sources (Gates-Grubstake Fund).

The obvious way to increase membrane permeance was to decrease the thickness of the silica deposit layer which represented about 80% of the resistance to permeation. The layer thickness depends on the penetration depth of the silica precursor within the pores of the tube wall. One way to decrease the penetration depth is to use silica precursors of higher reactivity. In our previous studies we used the silica precursors $SiCl_4$, $Cl_3SiOSiCl_3$, $Cl_3SiOSiCl_2OSiCl_3$. A literature survey revealed that one of the most reactive agents for liquid phase silylation is trimethylsilyl triflate ($(CH_3)_3SiOSO_2CF_3$). To grow a SiO_2 layer one would need to use the chloride analog $Cl_3SiOSO_2CF_3$. To this end we synthesized this analog and measured the reaction rate with Vycor glass in a thermogravimetric analyzer (TGA). It turned out that the reaction was too slow compared with the reactions of $SiCl_4$ and the other silylating compounds used previously. Evidently, reaction of the gaseous reagent with the pore surface is sterically hindered and also lacks the stabilization of the transition state afforded by the solvent in liquid phase reaction.

In view of the negative results the emphasis on different silica precursors was abandoned in favor of exploring different deposition conditions. The first modification was to use alternating rather than simultaneous reaction with $SiCl_4$ and H_2O. The second modification was to introduce carbon masks as means of decreasing the reactant penetration depth. These two techniques, and particularly the second one, resulted in dramatic improvements of membrane permeance as will be described in the following sections.

PROJECT DESCRIPTION

Alternating Reactants Deposition

Our previous membrane preparations[1-3] were carried out by one-sided CVD of SiO_2 on porous Vycor tubes using $SiCl_4$ (or some other related compound) and H_2O as the reactants. This standard deposition technique suffers from two disadvantages. The first is the development of nonuniform deposit layer thickness caused by depletion of $SiCl_4$ in the direction of flow. The second is formation of small clusters or particles in the gas phase by the direct reaction between $SiCl_4$ and H_2O, and subsequent deposition of these particles on the external surface of the support, causing additional thickening of the deposit layer. To avoid those two drawbacks of one-sided CVD we introduced the alternating reactants CVD. This new technique of membrane deposition entails two elements. The first element is the alternating rather than simultaneous contact of the support with the two reactants. The alternating contact completely eliminates formation of particles by gas phase reaction. The second element is the introduction of $SiCl_4$ into the evacuated reactor volume in discrete dosages rather than in continuous flow. Introduction of $SiCl_4$ into the evacuated volume eliminates or greatly reduces deposit layer nonuniformities. At the same time, limiting the dosage of $SiCl_4$ introduced in each cycle, reduces the penetration depth into the support.

The deposition reactor has been described in earlier publications. Briefly, it consists of an external quartz tube (11 mm ID) surrounding a concentrically placed porous Vycor tube (7 mm OD, 4.8 mm ID, 40 Å mean pore diameter) welded on both sections with nonporous quartz sections for convenient connection with inlet and outlet flows. The reactor is placed inside a split-tube electrical furnace. The reactant streams $SiCl_4$-N_2 and H_2O-N_2 were generated in bubblers at controlled temperatures. The $SiCl_4$-N_2 stream was stored in a large storage flask from which it was admitted intermittently into the reactor.

A membrane deposition experiment consisted of several consecutive silylation-hydrolysis cycles at reaction temperature 700-800°C. Each cycle entailed evacuating the reactor, admitting a dosage of $SiCl_4$-N_2 (the dosage being controlled by the

mol fraction of $SiCl_4$ in the storage flask) and allowing it to react for 1 minute, evacuating the reactor, and finally passing continuously a stream of H_2O-N_2 for 5 minutes. After each cycle, the permeance of N_2 was measured and when that permeance dropped below a preassigned level (lower by a factor 30-100 than the initial permeance), the deposition was terminated and the permeance of H_2 and N_2 were measured at several temperatures.

Selected membrane tubes were annealed at 500°C under 3 atm of H_2O (and 7 atm N_2) for several days to test their stability under expected operating conditions. After the hydrothermal treatment, the permeance of H_2 and N_2 were measured once more at several temperatures.

CVD Assisted by Carbon Barriers

A new technique developed in this project is the use of temporary carbon barriers to reduce the thickness of the deposit layer. The technique of carbon barriers involves first forming a thermosetting polymer inside the pores of the support, carbonizing the polymer, conducting SiO_2 deposition by one-sided or alternating CVD, and finally removing the carbon barrier by oxidation.

The polymer selected for these experiments was polyfurfuryl alcohol (PFA) which upon carbonization is known to undergo about 40% weight loss. The polymer was formed by polymerization of the furfuryl alcohol monomer (FA) using para-toluene sulfonic acid as the polymerization catalyst. After polymerization and cross-linking at 100°C for 24 hours, the support tube was heated slowly to 600°C to prepare it for CVD. Silica CVD was carried out by alternating deposition as described in the previous subsection. Finally, the carbon barrier was removed by oxidation with pure oxygen at 600°C for 18 hours. The permeance of H_2 and N_2 were measured after carbon deposition, after CVD and after the final oxidation step.

RESULTS

Alternating Deposition

Figure 1 shows the evolution of hydrogen and nitrogen permeance (based on the external diameter of the support tube) of two membranes formed by alternating CVD, one at 700°C and the other at 800°C. In each case the permeances were measured at the deposition temperature. Membrane 2 which was prepared at 800°C required a smaller number of cycles, had higher H_2:N_2 selectivity but somewhat lower H_2 permeance. These results can be attributed to a thinner but denser deposit layer at 800°C.

The two membranes shown in Figure 2 were heated at 500°C under 3 atm of H_2O (and 7 atm of N_2) for two weeks. Table 1 shows the change in the hydrogen and nitrogen permeances during this treatment. Table 2 shows the results of the same hydrothermal treatment in terms of the net permeance of the deposit layer, i.e. after subtracting the resistance of the bare support tube. Hydrothermal treatment decreases the permeances of the deposit layer by about 10% at 700°C and 50% at 450°C. The dependence of the reduction factor on temperature is due to the fact that hydrothermal treatment increases the activation energy. It is also seen that the membrane prepared at 800°C undergoes a slightly smaller change during hydrothermal treatment. These differences become more clear by looking at the activation energies for hydrogen permeation shown in Table 3. After deposition, membrane 2 has activation energy of 20.1 kJ/mol versus 17.3 of membrane 1. During hydrothermal treatment, however, the activation energy of both membranes increases and reaches a common level of 26 kJ/mol.

Comparison of the permeances shown in Tables 1-3 with the permeances of membranes prepared in our previous work by one-sided deposition reveals the following differences. The layers deposited by alternating reactants CVD have higher activation energies (17-20 kJ/mol vs. 10-12 kJ/mol) but approximately equal hydrogen permeances implying that the layers are thinner and denser. Upon hydrothermal treatment all layers are densified to the same final state with activation energy about 26 kJ/mol. As a result of this

densification, the permeance (at 600 K) declines by a factor 1.6 to 1.9 for the layers prepared by alternating deposition. The decline factor for the layers prepared by one-sided deposition is much higher, about 15. These large differences refer to the permeance of the deposit layer. The differences are much smaller for the permeance of the whole membrane tube because of the significant resistance of the support.

CVD Assisted by Carbon Barriers

Table 4 shows the H_2-permeance of a membrane prepared with the help of carbon barriers. The permeance for the whole tube and the net permeance of the deposit layer are listed. The activation energy for the permeance of the deposit layer is about 26 kJ/mol, essentially the same as that of layers prepared by one-sided deposition. Table 5 compares the permeance of layers prepared with and without the help of carbon barriers. Using the carbon barriers increases the deposit layer permeance by a factor of about 5.

FUTURE WORK

The practical result of using alternating deposition and carbon barriers is to increase the hydrogen permeance of the deposit layer by a factor of about 20 over the permeances obtained in our previous work. At 600 K the resistance to permeation due to the deposit layer is only 12% of the overall resistance, with 88% of the resistance residing on the support tube. To fully exploit the increased permeance of the deposit layer it is essential to use support tubes of lower resistance. One possibility is to use Vycor tubes of the same pore size as in the reported experiments but having smaller diameter and wall thickness. Reducing the wall thickness from 1.1 mm to 0.4 mm (corresponding to tubes with 0.2 mm ID) would increase the overall hydrogen permeance at 500 K from 0.68 to 1.26 $cm^3/cm^2/min\text{-}atm$, based on the inside diameter of the tube. Using as supports composite mesoporous/macroporous tubes like the ones marketed by US Filter, the overall permeance at 500 K can be increased to about 3.8 $cm^3/cm^2\text{-}min\text{-}atm$. These higher permeances are well above the economic viability threshold identified in the background section.

A number of issues need to be addressed in future work to demonstrate the commercial feasibility of the silica membranes. A critical need is the development of technology for fabrication of multitube modules. It is also important to demonstrate the preparation techniques using as supports smaller diameter Vycor tubes or composite mesoporous/macroporous tubes. Finally, the membranes should be tested for stability over longer periods of time.

REFERENCES

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2. Gavalas, G. R. 1993. Hydrogen Separation by Ceramic Membranes in Coal Gasification, DOE/METC DE-AC21-90MC26365, Final Report.

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Table 1. Permeance of Membranes Deposited on the Inner Surface Before and After Hydrothermal Treatment for 15 Days at 550°C under 3 atm H_2 and 7 atm N_2. The Dosage of $SiCl_4$ per Cycle was 0.28 μmol/cm^2.

			Permeance (cm^3(STP)/min atm cm^2)			
	Reaction T (°C)	Measurement T (°C)	After Deposition N_2	After Deposition H_2	After Treatment N_2	After Treatment H_2
Membrane 1	700	700	0.0039	0.38	0.00042	0.33
		600	0.0036	0.37	0.00015	0.30
		450	0.0019	0.33	0.000094	0.21
Membrane 2	800	800	0.0013	0.37	0.00033	0.34
		600	0.00046	0.34	0.00018	0.28
		450	0.00020	0.28	0.00015	0.19

Table 2. Permeance of Deposit Layers Excluding the Resistance of Vycor Tube. The Permeance is Given After Deposition and After 15 Days at 550°C under 3 atm H_2 and 7 atm N_2.

			Permeance (cm^3(STP)/min atm cm^2)			
	Reaction T (°C)	Measurement T (°C)	After Deposition N_2	After Deposition H_2	After Treatment N_2	After Treatment H_2
Membrane 1	700	700	0.0041	1.74	0.00042	1.04
		600	0.0037	1.33	0.00015	0.70
		450	0.0019	0.82	0.000094	0.34
Membrane 2	800	800	0.0013	1.65	0.00033	1.16
		600	0.00046	0.99	0.00018	0.63
		450	0.00020	0.56	0.00015	0.29

Table 3. Activation Energy for H_2 Permeance of the Deposit Layers in Membranes 1 and 2 Before and After Hydrothermal Treatments for 15 Days at 500°C under 3 atm H_2O and 7 atm N_2

	Activation Energy (kJ/mol)	
	After Deposition	After Treatment
Membrane 1	17.3	25.8
Membrane 2	20.1	25.8

Table 4. Hydrogen Permeance of a Silica Membrane Prepared With Alternating CVD and Carbon Barrier With and Without the Resistance of the Support Tube

	H_2 Permeance, $cm^3(STP)/cm^2$-min-atm		
Temperature, °C	Support Tube Plus Deposit Layer	Support Tube	Deposit Layer
450	0.667	0.867	2.90
523	0.679	0.824	3.85
600	0.692	0.787	5.75
700	0.687	0.745	8.56

Table 5. Comparison of Deposit Layer Permeances of Membranes Prepared by Alternating CVD With and Without the Use of Carbon Barrier

	H_2 Permeance, $cm^3(STP/cm^2$-min-atm	
Measurement T °C	Membrane Prepared without Carbon Barrier	Membrane Prepared with Carbon Barrier
450	0.62	1.88
600	1.13	3.74
700	1.57	5.57

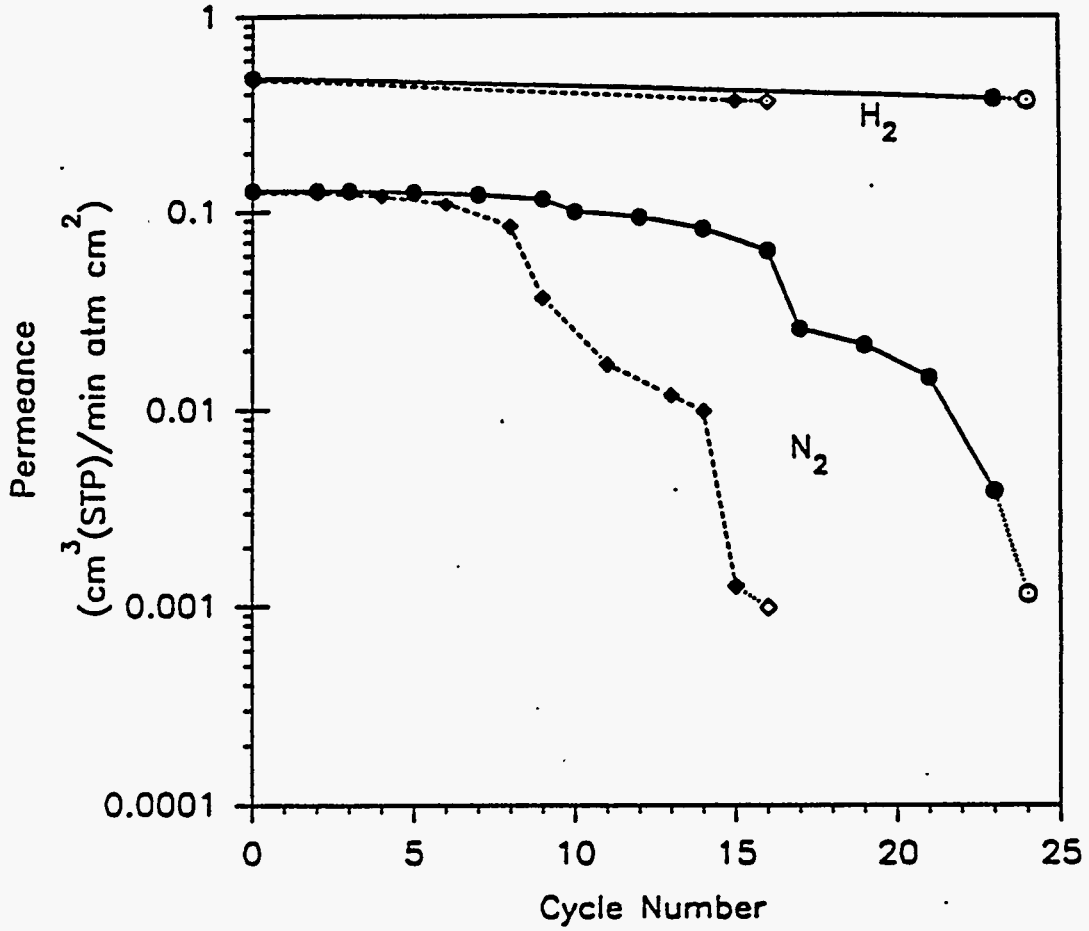

Figure 1. Permeances of H_2 and N_2 Versus Cycle Number for the Reaction at 700°C (Membrane 1. •) and 800°C (Membrane 2. ♦). Using $SiCl_4$ Dosage of 0.28 μmol/cm² per cycle. (◊) and (o) Indicate the Permeance Changes After 5 Days of Hydrothermal Treatment at 500°C under 3 atm H_2O and 7 atm of N_2.